Optical Fiber Tip Functionalized by Colloidal Photonic Crystal and Gold Nano-Particles for SERS Sensing

Lucia Sansone
Institute for Polymers, Composites and Biomaterials (IPCB), Consiglio Nazionale delle Ricerche,
Portici, Italy
lucia.sansone78@gmail.com

Marianna Pannico
Institute for Polymers, Composites and Biomaterials (IPCB), Consiglio Nazionale delle Ricerche,
Pozzuoli, Italy
marianna.pannico@ipcb.cnr.it

Pellegrino Musto
Institute for Polymers, Composites and Biomaterials (IPCB), Consiglio Nazionale delle Ricerche,
Pozzuoli, Italy
pellegrino.musto@ipcb.cnr.it

Stefania Campopiano
Deptment of Engineering University of Naples Parthenope
Napoli, Italy
campopiano@uniparthenope.it

Michele Giordano
Institute for Polymers, Composites and Biomaterials (IPCB), Consiglio Nazionale delle Ricerche,
Portici, Italy
michele.giordano@cnr.it

Agostino Iadicicco
Deptment of Engineering University of Naples Parthenope
Napoli, Italy
iadicicco@uniparthenope.it

***Abstract*—This work explores metal-dielectric colloidal crystal (MDCC) structures as SERS sensing layer. The MDCCs are fabricated directly onto optical fiber tip surface by successive depositions of PS Colloidal Crystal (CC) and Au NanoParticles. The fiber device is explored as remote SERS probe in optrode configuration. The MDCC permits to combine localized surface plasmon resonance (LSPR) of noble metallic nanoparticles and photonic bandgap (PBG) of colloidal type photonic crystals (PhCs). For the sensing test, the fiber probes were immersed in a 100μM aqueous solution of Rhodamine (R6G). Then, preliminary SERS results were retrieved by a Labspec Aramis confocal Raman spectrometer.**

Keywords—SERS, optical fiber sensors, remote sensing optrode probe.

I. INTRODUCTION

Surface enhanced Raman scattering (SERS) has been emerging as an important sensing tool for the high sensitivity detection of analytes in diverse challenging fields including biomedicine, food chemistry, security, and many others [1].

In such approach, the intrinsic recognition capabilities of Raman effect are combined with capability of speciality substrates to locally enhance the electrical field. The result of this mechanism is the capability to read Raman signal of small volume of analyte which normally cannot be read at all [2].

So far, several aspects related to the practical application of SERS effect in real scenario are investigated from different research groups. For instance, a lot of groups are involved in the study of the origin of the SERS effect. Other researchers are focused on the design and development of simple setup for reading of SERS signal to make it a point-of-care sensing tool.

The design and development of novel substrates capable to locally enhance the electrical field is the main issue for enabling the widespread diffusion of SERS [3]. It demands efficient substrates reproducible, and possibly mass producible. Novel designs of the SERS sensing layer is one of the most important subjects in the development of new SERS sensors [4]. The quality of sensing layer results in the sensitivity and selectivity of a SERS detector.

Moreover, SERS optical fiber sensors combine the SERS substrate with optical waveguide, which allow the applications for in situ and remote SERS detections [5], [6]. Different approaches have been proposed for engineering optical fibers for SERS and can be divided into two main groups: optrodes and cladding-coupled sensors. The last ones usually leads to very fragile sensors, and the re-coupling of the Raman scattered light is very inefficient, resulting in limited Raman sensitivity [7].

For the optrode approach, there are many literatures referring to the fabrication techniques of the SERS sensing layer on the optical fiber tip. Most of them are based on the methods of preparing SERS substrates [8]–[12]. G. Quero et al. presented an engineered lab-on-fiber SERS optrode by nanosphere lithography approach [9]. Xu et al presented a taper-fiber modified by gold nanoparticles with ultrathin alumina layers as SERS nanoprobe [11]. Lan et al. discussed on an alternative method to fabricate SERS fiber via direct femtosecond laser ablations resulted in nanostructures on the cleaved end face of a multimode optical fiber with a 105/125 μm core/cladding diameter [12]. Lucotti et al presented engineered fiber tip shape (fabricated by a quasistatic chemical etching protocol) [8].

In this scenario, we explore metal-dielectric colloidal crystal (MDCC) structures as SERS sensing layer [13], [14]. The MDCCs consist of self-assembled PS Colloidal Crystal (CC) of PS nanospheres with diameter of 242 nm exhibiting a photonic bandgap at about 520nm integrated with Au nanoparticles (AuNPs) of diameter about 23 nm. The MDCC permits to combine localized surface plasmon resonance (LSPR) of noble AuNPS and photonic bandgap of colloidal type photonic crystals (PhCs). Moreover, in this work, MDCCs are fabricated directly onto optical fiber tip surface by successive dep-coating procedure enabling to fabrication of remote SERS probe. A schematic view of fiber probe is

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plotted in fig. 1. SERS performance in optrode configuration have been investigated by immersion of the fiber probe in aqueous solution of Rhodamine (R6G) at concentration of 100μM.

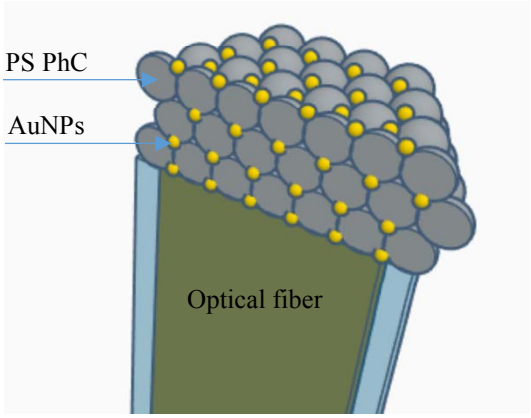

Fig. . Schematic of the MDCC onto optical fiber tip

II. Sample Fabrication

MDCCs were fabricated directly onto optical fiber tip. Here we selected multimode optical fibers with core/cladding diameter of 105/125 μm and NA of 0.22. The fiber has a double role: the fiber tip represents an unconventional substrate to realize SERS layer; at same time fiber represents the communication channel for the excitation laser and Raman signals. During the fabrication, step-by-step the reflectance spectra were measured by illuminating the fiber tip with a xenon optical source (OceanOptics HPX-2000 185-2000nm) and redirecting the reflected light to an optical spectrum analyzer (OceanOptics, HR 2000+) by means of a lab-grade 3dB fiber splitter: a schematic view of the optical setup schematically plotted in fig. 2 [15].

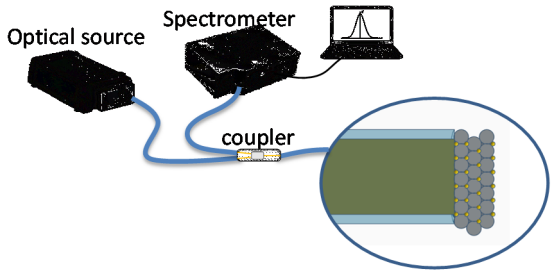

Fig. 2 Optoelectronic setup for reflectance spectra meausremnts.

For the aim of this paper, PS nanospheres with diameter of about 242 nm were synthesized through a free surfactant emulsion polymerization technique. Polymerization reaction was carried out in 3- neck round flask under 250 rpm at 70 ºC for 5 hours. Purified styrene was added into distilled water at constant temperature. The polymerization processes were started by adding KPS under nitrogen flow. The mixture was cooled down to room temperature and irradiated using sonication processor probe for 15 minutes. Figs. 3(a) shows two SEM Micrographs at different magnifications.

AuNPs were synthesized via the citrate reduction method: a 100 mL sample of aqueous $HAuCl_4$ (0.25 mM), was put into a 250 mL flask at room temperature. After the solution was brought to boil while magnetically stirring (400 rpm), 0.7 mL of 5% w/w sodium citrate solution was added. The reaction was allowed to run until the solution became wine red in colour. The AuNPs concentration is 2,5 nM assuming 100% conversion of $HAuCl_4$ to AuNPs. A TEM microscopy image is plotted in Fig. 3(b).

The fabrication of fiber probe consists in few steps mainly based on dip-coating operations.

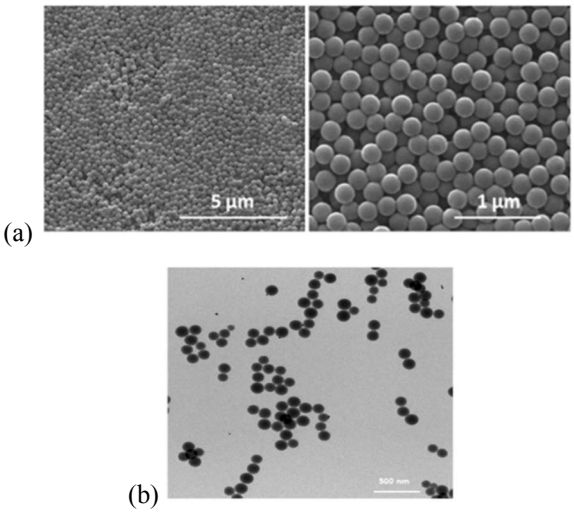

Fig. 3. (a) SEM Micrographs PS nanospheres of 242 nm acquired at two different magnifications; (b)

The first one is the fiber cut: fiber tip flatness is vital to fabricate defect-free SERS layer.

Successively, a chemical treatment of the fiber tip surface is provided to favorite the steady CC self-assembling: fiber tips were immersed in a solution of APTES in ethanol at 5% for 3h.

The CCs on optical fiber tip were achieved by dip-coating vertical deposition technique from 0.1% w/w water solution of PS spheres [13], [16]. The fig. 4(a) plot reflectance spectra of the bare fiber tip (selected as reference) and after PS PhC deposition. The formation of PBG i.e. reflectance peak, centered at 520nm, is well evident: here maxim reflectance reaches 173 % whereas reflectance out of band (900-1000 nm) decreases to 24 %.

Finally, AuNPs are added by successive dip-coating operations. It is expected that the gold nanoparticles are immobilized inside the PS lattice (see schematic in fig.1). AuNPs are small enough to be included in the interstices of opals without perturbing their structure. The number of AuNPs is a crucial parameter for the performance of the SERS probe. In this work 5 dip-coating operations are carried out to increase the AuNPs inside the lattice structure. However, it represents a future parameter to be investigated for optimization. The reflected spectra after each dip-coating is added in fig. 4(a). It is evident that the reflectance decreases with the increases of AuNPs dip-coating. Reflectance maximum intensity reduces of about 25% after 5 dip-coating in gold solution. To better understand the effect of gold, the spectra normalized to the spectrum of the fiber with PhC (before gold) are plotted in fig. 4(b). It is evident that maximum reduction is achieved at 690 nm.

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III. SERS RESULTS

To test the SERS performances of the fiber probe R6G was dissolved in milli-Q water to prepare solutions with concentrations of 10^{-4} M. For Raman experiments on the fiber, the Raman spectrometer was coupled to the optical fiber in optrode configuration as schematically represented in Fig. 5. The fiber SERS probe was cut into segment of 20 cm with a flat end surface for laser injection and was vertically mounted under the microscope. An adaptive fiber-optic holder was built in order to suitably couple the laser radiation to the fiber tip surface keeping it vertically.

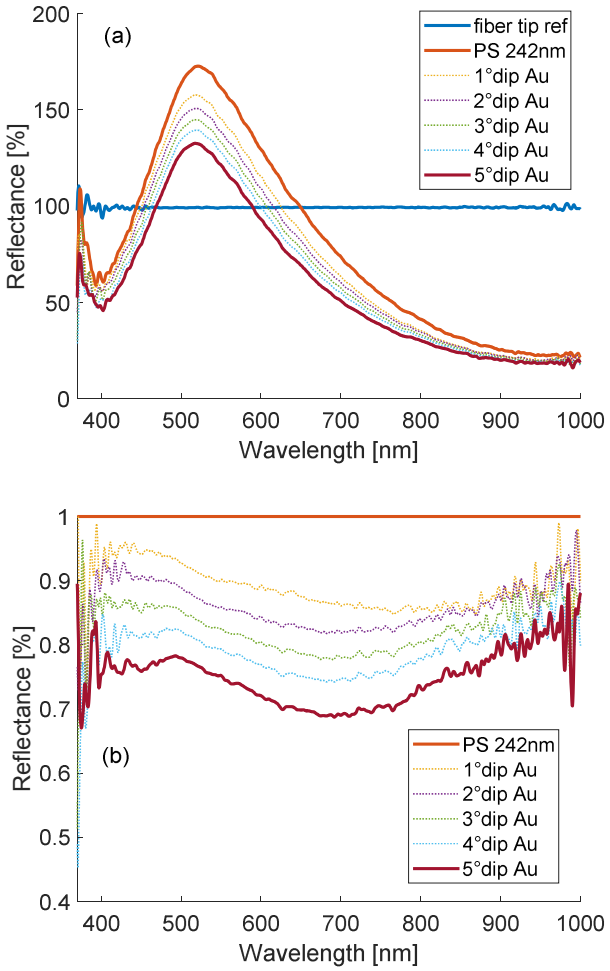

Fig. 4. (a) Reflected spectra of sample with PS of 242 nm during fabrication process; (b) Reflected spectra normalized to PhC spectrum.

The fiber was back excited by the 632 nm laser beam trough the fiber flat end surface. A 10x objective (MPlan, NA = 0.25) matching the NA of the optical fiber (NA=0.22) was used to guide the laser beam onto the sample and for collecting the backscattered light. One spectrum was accumulated for each measurement and the exposure time was set to 20 seconds depending on the sample. The optrode SERS measurements were carried out in solution (DIP mode) and after drying (DIP&DRY mode). In DIP mode, the terminal SERS active fiber end was immersed in an aqueous solution of R6G at 10^{-4}M. The spectra were collected after 10 minutes immersion, an adequate time for R6G adsorption. In DIP&DRY mode, after 10 min immersion in the R6G solution, the fiber was dried at ambient conditions and after 3 minutes the spectra were collected. In order to keep consistency, the above experimental conditions were fixed for all the optrode Raman measurements.

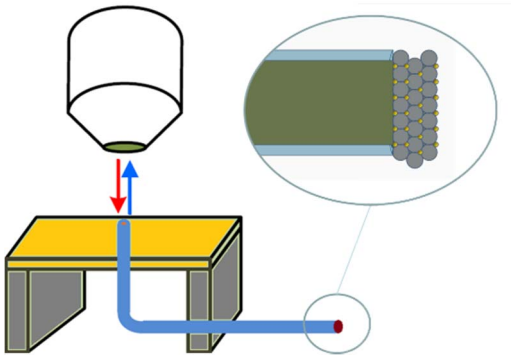

Fig. 5 A schematic representation of the experimental setup for the SERS measurements: (a) direct configuration; (b) optrode configuration

In order to ascertain the SERS performance of our sample we first collected the reference enhanced Raman spectrum of the AuNPS doped PhCs fibers, before the surface functionalization with R6G, in air and by dipping the fiber in a blank aqueous solution. Fig. 6 shows the R6G SERS spectra collected. All the spectra were corrected by subtracting the relative background spectrum (in air for DIP&DRY mode and in aqueous solution for DIP mode) and then smoothing was applied to increase the signal-to-noise ratio without altering the signal. The characteristic peaks of R6G are clearly observable at 1182, 1308, 1360, 1508, 1645 cm-1. According to literature, all these modes, but the one at 1308 cm-1, are in-plane deformations of the whole xanthene unit (cooperative C–C stretching of the condensed aromatic rings). The 1308 cm-1 vibration is a C–C–H bending [17]. In comparison IP&DRY and DIP spectra, iIt is apparent that DIP&DRY is a more efficient sampling mode, accordingly with literature. The same result was achieved for different R6G concentrations.

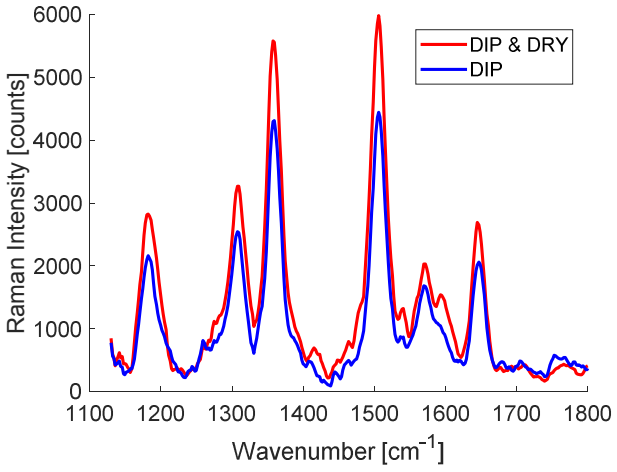

Fig. 6 SERS spectra of R6G collected in optrode configuration collected at 20 seconds: Comparison between the SERS spectra of R6G at 10^{-4} M collected in DIP&DRY mode (red trace) and DIP mode (blue trace).

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IV. CONCLUSIONS

This work is focused on the investigation in MDCC structures in excitation of localized plasmon resonance for SERS activities.

The MDCCs were achieved by self-assembled of 3D colloidal PS nanospheres enriched with gold nanoparticles (AuNPs). PS nanospheres with diameter of 242 nm were synthesized. The sample was enriched with AuNPS by successive 5 dip coating in gold nanoparticles solution. Here AuNPS with average diameter of 23.3 nm were synthesized and selected.

SERS performance in optrode configuration has been investigated by Raman spectrometer with the excitation wavelength of 633 nm and Rodamine (R6G) solution at concentration of 100 μM. We found that SERS activities is very well evident. Moreover, peak intensity in DIP and DIP &DRY mode are compared.

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